

## THE GLOW DISCHARGE DEPOSITION OF BORON

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## INTRODUCTION

Many new materials concepts are evolving out of aerospace materials technology. One of the most promising of these is that of boron filament-reinforced composite structures. Incorporation of continuous boron filament in a suitable matrix could yield a structure with the strength of high-strength steel, the rigidity of beryllium, and the density of magnesium. A large-scale development effort is currently concerned with fabrication of such structures. Once this has been achieved, large amounts of filament must be made available at reasonable cost to make large-scale usage practical. Present techniques for filament production are based on scaled-up laboratory chemical vapor deposition procedures, and major technological development is required to result in large-scale production. As a result, many other new and novel techniques for filament preparation have been investigated with the intent of developing alternate approaches.

This study is concerned with investigation of one such approach, that of deposition in an electrodeless glow discharge. Basically a high-voltage, low-amperage, high-frequency rf current is imposed across a boron-containing gas, resulting in a high degree of ionization/activation of the ions present. Boron then deposits out in elemental form on all surfaces within the glow discharge area. Use of proper deposition conditions confines the glow largely to the filament substrate. By passage of the filamentary substrate continuously through the discharge, the approach is potentially capable of high rate filament formation with excellent uniformity and reliability. Variation of current input can result in deposition at any point from room temperature up to 800–1000°C. Both metallic and non-metallic substrates can be employed. Deposition is achieved at low pressures of the order of a few mm.

The bulk of the work described has been carried out using a fixed filament system in order to study the effects of operating parameters. Work has also been confined to the hydrogen-boron trichloride system. The approach has been studied with respect to ratio of reactants, total system pressure, voltage, current, and type of substrate. The most recent work is concerned with development of a continuous system and adjustment of parameters to produce desired deposition characteristics.

Literature in the area of glow discharges is very extensive, but work on chemical reactions in discharges, such as are of concern to this work, is very limited. Some work has been done on effects of discharges on boron compounds together with a small amount of work on deposition of boron as amorphous powders.

Holzman and Morris (Ref. 1) have reported formation of  $B_2Cl_4$  from  $BCl_3$  in an electrodeless glow discharge.  $BCl$  was the principal intermediate in the course of the reaction. Kotlensky and Schaeffer (Ref. 2) have described decomposition of diborane in a low-pressure glow discharge to give higher hydrides of boron. Rosenberg (Ref. 3) has studied the reaction of boron halides with nonmetal oxides under the influence of electrical discharges. Markovskii et al. (Ref. 4) claim to have prepared elemental boron of 99.9% purity through reaction of boron trichloride and hydrogen in a glow discharge. However, efforts to duplicate this work indicate that the conditions employed lead to effects more like an arc than a glow discharge. Related, although distinctly thermally rather than electrically initiated processes, are the original arc preparations of pure boron as carried out by Weintraub (Ref. 5) and Kroll (Ref. 6). Other references to behavior of boron compounds in electrical discharges are given in the report of the International Symposium on Electrical Discharges in Gases (Ref. 7).

## EXPERIMENTAL WORK

**Apparatus.** The basic apparatus utilized for parametric studies employing a fixed substrate is shown in Fig. 1. The reaction vessel is a simple pyrex tube with the substrate filament suspended down the central axis and suitably sealed at each end. The reactant gases are admitted at one end of the tube and exit at the opposite end. Electrodes are simple concentric copper strips which may be moved along the tube for optimum positioning. The glow discharge then forms between these electrodes. Both horizontal and vertical reactor configurations have been employed; the vertical system is preferred since substrate alignment is better controlled. The vertical arrangement is also more amenable to moving filament systems for continuous filament preparation. Both air and water cooled reaction vessels have been evaluated. Water cooling was originally instituted to minimize sidewall deposition; later work demonstrated that this could be accomplished by regulation of gas composition and current input so as to confine the glow area to the central area of the reaction tube. A three compartment chamber was used so that these experiments could be performed before the system was opened for examination.

The balance of the system is largely a gas flow system. Hydrogen is passed through a catalytic cartridge and a liquid nitrogen trap for removal of oxygen and water impurities. Boron trichloride is fed into the hydrogen stream. Both lines have appropriate flowmeter devices. The boron trichloride is controlled at the cylinder valve; satisfactory control with respect to potential condensation is obtained by bleeding the gas into a section of tubing at operating pressures and heated to 35°C. Hydrogen flow is regulated by a stainless steel needle valve just downstream from the flowmeter. The combined hydrogen-boron trichloride stream then passes into the reaction chamber. Exit gases from the reactor pass successively through a trap for condensation of unused boron trichloride, past a manometer, through a Cartesian manostat, and thence to a mechanical vacuum pump.

The power supply is a Lockheed-designed 3 Mc oscillator capable of about 30 W output; however, only a portion of this output is available as rf power, about 20 W at 1400–1500 V. The first 20 turns of the large coil (Fig. 1), and the capacitance connected across them, act as the tank. The tank is a resonance combination wherein the energy is alternately stored in the condensers and in the field of the coil, with interchange occurring at a frequency determined by the coil inductance and capacitance of the condensers. A variable condenser included in the tank allows its frequency to be matched to that of the secondary. When such matching occurs, the coils are efficiently coupled, and rf power is drawn from the secondary. This power is fed into the primary by a 6146A transmitter tube activated at proper frequency by feedback from the tank. This is done through a condenser and a resistor wound with a coil, serving as a low-Q resonance circuit to suppress high frequency parasitic oscillation. A 47K resistor allows the grid to be self-biased. An rf choke prevents loss of power into the backup power supply. Two 10K resistors and a 7500  $\Omega$  resistors serve as a voltage divider for the screen grid.

**Materials.** The boron trichloride used was electronic grade supplied by American Potash and Chemical Co. Hydrogen was a high purity laboratory grade (BB-H-886) supplied by Air Reduction Co. Quartz monofilament utilized as a substrate for most of the work was obtained from the General Electric Co. Glass filaments were drawn from pyrex glass rods by the LMSC glass shop.

**General Procedure.** Experiments were started by evacuating the assembled apparatus to 1 mm Hg pressure. The leak rate was determined by turning off the pump and noting the increase in pressure over extended time periods. A leak rate of less than 0.05 mm Hg/min is necessary to avoid boron oxide formation. When the system was determined to be essentially leak free, a flow of hydrogen was introduced and allowed to sweep through the apparatus for 15 to 30 min. The desired gas pressures and flow rates of hydrogen and boron trichloride were established, the power supply for the oscillator turned on, and the flow was initiated by adjusting the variable capacitor. At the end of the experiment, the flow discharge and the boron trichloride flow were turned off and hydrogen allowed to sweep through the

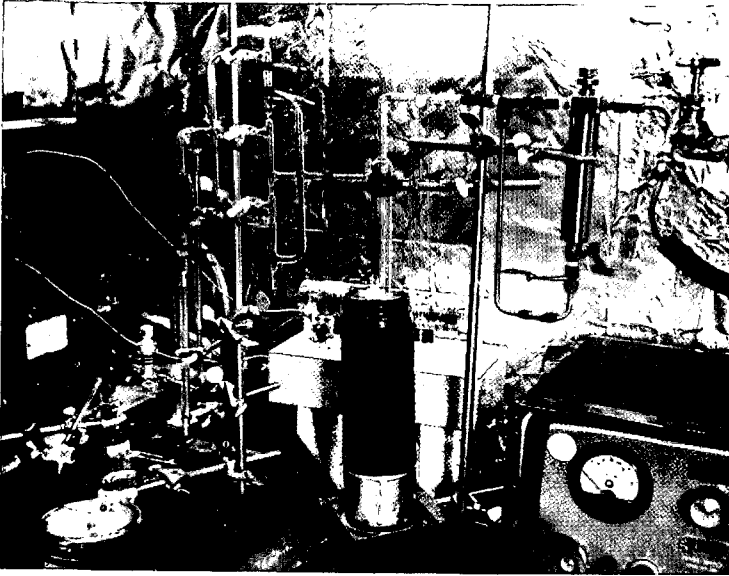
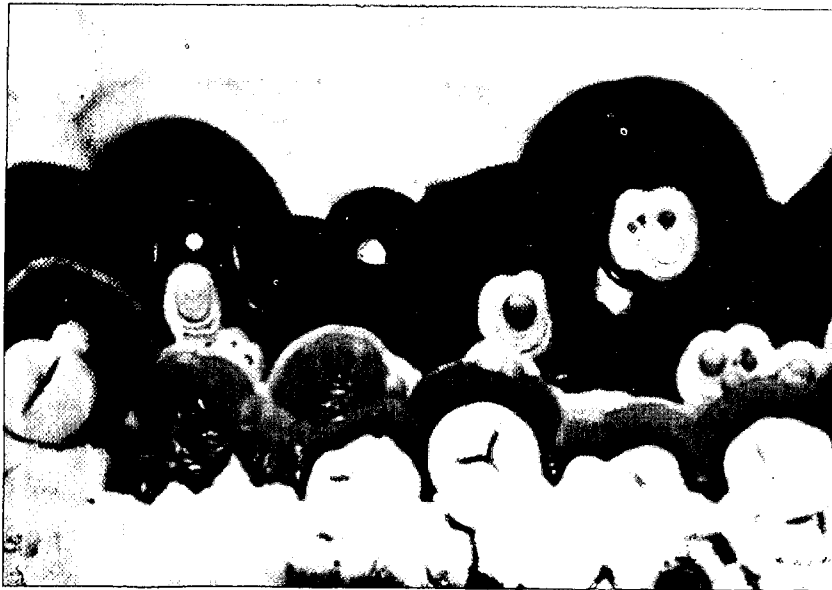


Fig. 1 Process Apparatus



Boron

$B_2O_3$

Oxygen  
Enriched  
or  
Oriented  
Material

Boron

Fig. 2 Boron on Glass, Longitudinal Section (3000 $\times$ )

apparatus for 10 min to remove unreacted boron trichloride. The pump was turned off and the apparatus returned to ambient pressure using hydrogen. The apparatus was then dismounted and the sample removed.

## RESULTS

**Preliminary Experiments.** Initial experiments were made to observe operating characteristics while exciting hydrogen gas in a glow discharge. Glow discharges were initiated in hydrogen at pressures of 6, 15, 36, 40, 60, and 81 mm Hg and at flow rates of about 40 to 100 cc/min. Electrode separations of 0.75, 1.0, 2.0, 3.5, and 4.5 cm were used. The glow was initiated by tuning the capacitor at maximum voltage to obtain an input current of 105 mA. The effect of power input to the oscillator on the glow discharge was determined by varying the voltage. The change in glow is reflected in the current drawn by the oscillator at any particular voltage and capacity setting. The following characteristics were observed:

- Increasing gas-flow rates reduces the glow intensity.
- Increasing pressure reduces the glow intensity.
- In general, glow intensity is reduced as the electrode distance is increased.

Glow was maintained in the presence of a dielectric and a conductor filament to determine their effect on glow characteristics. The presence of a strand of quartz, QFY-150 to 204 end, 1/0, with oil starch finish,  $d = 0.004$  in., did not affect the operating characteristics of the glow. However, the presence of a 5-mil tungsten wire resulted in considerable changes in the glow. The tungsten wire acted as a ground connection, and the ground lead from the oscillator could be disconnected without affecting the glow. The glow was concentrated at and spread out along the wire. This system used much higher currents and, as a result, considerable heat was generated. A mirror was deposited on the reaction tube walls.

A series of experiments were performed using glass and quartz substrates to determine approximate conditions necessary for the deposition of boron. A qualitative description of the process was obtained from these observations. The data shown in Table I describes the experimental conditions along with pertinent observations. The results have been summarized in the following qualitative statements:

- Wall deposition is favored by high hydrogen and low  $\text{BCl}_3$  flow rates.
- Deposition on the filament substrate is more pronounced at higher flow rates of  $\text{BCl}_3$ .
- Use of a water cooled reactor lowers wall deposition.
- Small leaks of air result in the formation of the oxide rather than the metal (see experiment 07-18A and Fig. 2).
- Under certain conditions of power input and gas flow, a brown deposit is formed that hydrolyzes on exposure to air and evolves a gas (see experiment 07-20A and 07-21A).
- Thick deposits of boron can be produced in reasonable times and conditions (see Fig. 3).

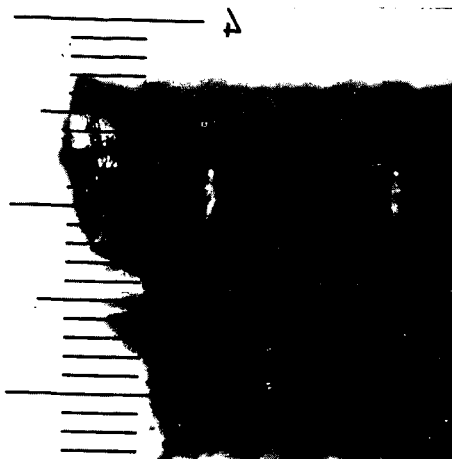
Following these preliminary experiments, flowmeters were calibrated and the quartz monofilament substrate was characterized in terms of physical and mechanical properties. A study was then initiated on effects of the various process parameters.

**Parametric Study.** A study of the effect of process parameters on the deposition of boron using the static filament apparatus was conducted. The parameters studied include system pressure, reactant gas flows and ratios, electrode separation and configurations, and field strengths. The evaluation of certain parameters has been quantitative and was based on the weight of boron deposited or on the thickness of the deposit at the midpoint of the filament. Other parameters were evaluated by a qualitative description of the deposit.

Table I

## DEPOSITION OF BORON IN GLASS AND QUARTZ SUBSTRATES

Experiment	Manometer pressure (mm Hg)	BCl <sub>3</sub> flow reading (mm)	H <sub>2</sub> flow reading (mm)	Direct current to oscillator (mA)	Reaction time (min)	Results
07-13A	2.0	6-7	5-8	75	75	Medium deposit at electrodes; light deposit between electrodes.
07-13B	2.0	6-7	3.5	95 75	15 15	Heavy deposit on walls.
07-13C	2.0	6.5	6.5	75 90	60 30	Heavy deposit on walls near electrodes.
07-13D	2.0	14	2.5	75 90	100 20	Very heavy deposit on walls.
07-13E	2.0	14	7	90	75	Medium deposit on walls.
07-13F	2.0	3.5	14	90	25	Glass filament heated; light deposit on walls.
07-13G	2.0	(Initial) 1.0	10	-	15	As H <sub>2</sub> is depleted, glow turns white, then green, then goes out.
07-17A	40	2.0	2.0	150	40	Water-cooled reactor; smooth thin coating.
07-18A	25	1.5	9.0	110	25	Rough thick metallic appearing (see Fig. 2), leak developed during run, was repaired and run completed.
07-20C	25	1	4	80	30	Brown non-metallic deposit which hydrolyzes in air.
07-21A	25	4.0	9.5	80	10	Metallic (see Fig. 3).



(a) Filament Emerging From Broken End (220×)



(b) Surface of Deposit at Broken End (220×)

Fig. 3 Boron on Quartz

This study is only an approximation of the moving filament system. The movement of the filament in a continuous system averages the effects of all the parameters so that the filament sample is prepared in a uniform manner. The edge effects noted on the filament situated under the electrodes would not be evident in a continuous system.

Material efficiencies are based on the amount of boron produced from the total amount of boron passed through the reactor. The electrical efficiency is based on the amount of boron produced divided by the theoretical amount that could be produced by the total charge passed using the reduction equation  $B^{+3} \rightarrow B^0 + 3e$ . The current was measured by an rf ammeter placed in the electrical circuit.

### (1) Electrode Configuration

The experiments performed previously have used electrodes made from copper foil. The electrodes are shown in Fig. 4. It was the purpose of one of the series of experiments conducted to determine if other electrode configurations would be desirable. The configurations shown in Figs. 4b, 4c, 4d, and 4e were used. The following qualitative observations were sufficient for determining the best design at this time:

- The plate electrodes parallel to the gas flow shown in Fig. 4 produce a glow but no boron deposition with gas flows and reactant concentrations known to deposit boron when ring electrodes are used.
- The large sheet electrodes shown in Fig. 4d encourage the deposition of boron on the side walls between the electrodes.
- Electrodes, using No. 16 copper wire, hooked up as in Fig. 4a produce a minimal amount of sidewall deposition, and influence of the electrodes on the deposit underneath is also reduced.
- Electrodes, using No. 16 copper wire, hooked up as in Figs. 4b and 4c produce uneven glows and deposits. The glow will be intense between two of the electrodes while the glow between the other electrodes is very faint. The conductivity of the gas phases, electrode separation, and limitation of the current output of the oscillator are probably important factors.

On the basis of the results observed, copper wire electrodes wound around the reactor tube as in Fig. 4a have been used in the process study.

### (2) Electrode Separation

The effect of electrode separation on the deposition of boron is shown in Table II. The gas flow, reactor pressure, and electrical parameters were the same in all cases. The data show a rise in efficiency as the electrode separation is increased to 2.54 cm.

Table II

EFFECT OF ELECTRODE SEPARATION

Electrode distance (cm)	Deposit length (cm)	Deposit weight ( $\mu\text{gm/cm}$ )	Total thickness (mils)	Material efficiency	Electrical efficiency
0.62	0.85	35.3	1.8	0.34	0.76
2.22	2.15	23.4	1.67	0.59	1.52
3.16	2.22	25.3	1.72	0.66	1.41
2.54(a)	2.15	46.5	2.22	1.15	2.55

(a) Reactor walls grooved at electrode positions.





Increasing the distance beyond this does not increase the efficiencies or the length of substrate upon which deposition occurs. The last experiment shown in this table indicates considerable improvement in efficiencies at 1-in. electrode distances. The reactor is pinched at the electrode positions in this experiment so that the gas stream is forced closer to the substrate. This results in considerable improvement in efficiencies.

### (3) Ratio of $\text{BCl}_3$ to Hydrogen

The ratio of  $\text{BCl}_3$  to hydrogen has very little effect on the efficiency of the reaction. This is shown in Table III. The increase in efficiency at the very low ratio is probably due to the use of the pinched electrode positions in the reactor walls. The efficiencies are so low, the quantities measured are quite small and the material efficiencies shown are not significantly different. In keeping with this observation, the electrical efficiency remains constant over this flow ratio range and indicates that the electrical energy is primarily used in activating atoms or molecules and producing electrons which then react with the other gases. Since hydrogen is the predominate gas it can be presumed that the particular frequency employed in the system results in ionization of the hydrogen.

Table III

#### EFFECT OF FLOW RATIO

Mole ratio $\text{BCl}_3/\text{H}_2$	Reaction time (min)	Material efficiency (% per pass)	Electrical efficiency (% per pass)
0.22	7.80	0.046	1.2
0.19	5.0	0.044	1.1
0.12	10.0	0.06	1.1
0.08	20.0	0.14	1.2

As the mole ratio of  $\text{BCl}_3$  to hydrogen is increased from 0.22 to 0.66 (near stoichiometric) and by reducing the hydrogen gas flow, the appearance of the glow and the character of the deposit are changed significantly. The hydrogen flow rate is an estimated value because the calibration curve does not extend to these low flowmeter readings. However by cutting the hydrogen flow rate in half, making the flow rate near stoichiometric for the reaction, the glow is intensified around the filament substrate and will migrate along the substrate beyond the rf electrodes. The deposit character produced by this procedure is shown in Fig. 40. These pictures show the types of deposits that are formed at different points on the substrate.

The deposition rate is significantly affected by the flow ratio as shown in Table IV.

Table IV

#### EFFECT OF FLOW RATIO ON DEPOSITION RATE

Mole flow ratio $\text{BCl}_3/\text{H}_2$	Deposition rate (mils/min)
0.22	0.05
0.33	0.04
0.66 (est.)	0.19

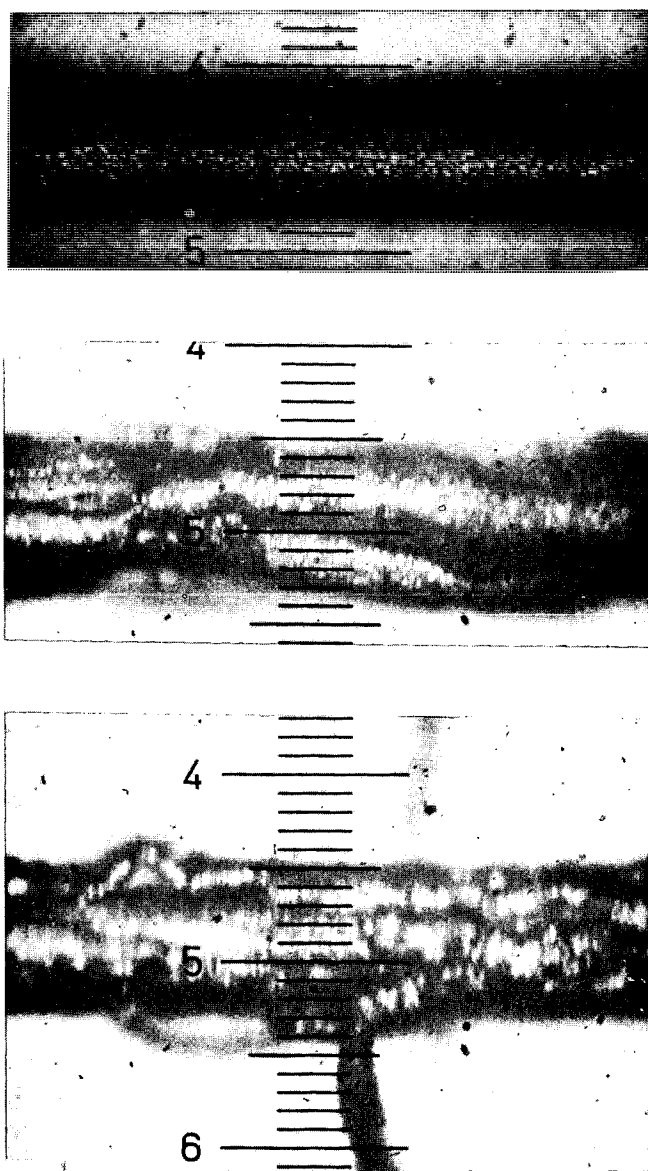


Fig. 5 Filaments Produced at Near Stoichiometric Flow Ratios (220 $\times$ )

#### (4) Effect of System Pressure

The effect of system pressure on deposit characteristics is shown in Table V.

Table V  
EFFECTS OF SYSTEM PRESSURE

Pressure (mm Hg)	Type of deposit
5	Needles, trees, and dendrites. Exploded from substrate if run was long
20	Thick, fairly uniform, some craters or knobs
30	Thick, small mounds, no craters

#### (5) Effect of Power Input

At all pressures and flow rates employed, a reduction in rf current by capacitance control, or a reduction in dc voltage results in a non-metallic, hydrolyzable material which is clear white in appearance.

#### (6) Interaction of Parameters

The gas phase being ionized is an integral part of the electrical circuit. Thus as gas composition, pressure, or electrode spacing is varied, the impedance of the gas phase is also changed. The necessary voltage and rf currents are thus changed. These changes are reflected in the type of deposit obtained.

### DISCUSSION

**General.** The results of these experiments show that boron can be deposited on a dielectric substrate in a glow discharge. There is no limit on the coating thickness inherent in the process. Complete control of the process parameters has not been achieved, but there is no reason to believe that control cannot be achieved. The results obtained so far indicate that gas purity, gas composition, and rf power input are among the most important factors.

**Gas Purity.** The deposit obtained can be considered to be in chemical equilibrium with the gas composition. The introduction of certain impurities such as oxygen or water will result in certain amounts of oxygen in the deposit. The solid solubility of oxygen in boron is probably not great, and its effect in the mechanical properties of the deposit is unknown. However, if a certain concentration of oxygen or water is present, the equilibrium solid phase resulting from the processing will be the oxide and not the element. Experimental experience has shown that this concentration value is probably not very great, and a tight process system must be used with the reduced pressure process.

**Gas Composition.** The effect of gas composition, i. e., the ratio of hydrogen to boron trichloride, will influence the type of reaction that occurs and the type of product formed. It has been observed that the amount of (1) sidewall deposition; and (2) fine particles that fall out of the gas downstream of the glow, increase with increasing hydrogen concentrations. This indicates that reduction in the gas phase increases with the higher hydrogen to boron trichloride ratios. With increasing hydrogen ratios, the glow is more uniform over the space and the formation of fine particles is encouraged.

Increasing the ratio of boron trichloride to hydrogen causes the glow to concentrate toward the center around the substrate. This concentration of the glow toward the center discourages

the formation of small particles by the boron atoms and encourages the growth of the coating by deposition of the boron atoms directly on the substrate. As the flow ratio approaches the stoichiometric value of 1.5 moles of  $H_2$  per mole  $BCl_3$ , the glow concentrates very close to the substrate and is observed to migrate along the filament beyond the electrode rings. At the same time the rate of deposition increases about fourfold or more.

The resistance of the filament decreases as the boron coating is formed, which allows more current to flow. This increases the temperature of the filament, which encourages more rapid deposition of boron. Under these conditions, the reaction goes out of control and the filament heats to a general red-orange glow with brighter spots and finally breaks.

Careful adjustment of the reactant gas concentration and the rf power input to the coil will minimize the gas-phase reaction, sidewall deposition, and fine-particle formation.

The gas composition also obviously influences the nature of the material deposited. The glow discharge of boron trichloride has been studied by several workers (Refs. 1, 5, and 8 to 16) in the field, and their results should indicate the deposit to be expected at high ratios of boron trichloride to hydrogen. Holzmann and Morris (Ref. 1) analyzed the light from glows of boron trichloride at 1 mm of Hg pressure. The glow discharges were caused by a  $2.4$  to  $2.5 \times 10^9$  Hz (2,400 to 2,500 Mc). They observed bands due to boron monochloride and lines due to atomic boron and atomic chlorine. Frazer and Holzmann (Ref. 9) have used this technique to prepare laboratory quantities of  $B_2Cl_4$ , which is the primary product under these conditions.

The compound  $B_2Cl_4$  can be decomposed under a variety of conditions. Rosenberg (Ref. 8) used 60-Hz 10-kV discharges in  $B_2Cl_4$  and obtained  $BCl_3(g)$  and  $(BCl)_n$ , which he described as a light brown or yellow film which is hydrolyzed by water to form  $B_2O_3$ , hydrochloric acid, and hydrogen. From the rather incomplete data on this system and from other authors, it appears that a  $(BCl)_n$  phase can be obtained at compositions down to  $(BCl_{0.9})_n$ , and a material which analyzes as  $BCl_{0.6}$  has been reported. At the present time the  $(BCl)_n$  material is considered to be a polymer, and a series of higher unit structures other than  $B_2Cl_4$ , (such as  $B_4Cl_4$ ) can also be obtained.

In addition to these considerations, experiments have shown that, by operating at reduced rf currents, a deposit possessing the reported properties of  $(BCl)_n$  can be obtained with gas compositions that would normally deposit elemental boron.

In summarizing the results and literature survey, it is possible by glow-discharge techniques to obtain a variety of products from boron trichloride and hydrogen gas streams. These products can range from a polymer-type  $(BCl)_n$ , a liquid  $B_2Cl_4$ , or a solid  $BCl_{0.6}$  to the boranes. In between these gas compositions that will give the foregoing products is the gas-composition range that will give boron as a product. In addition to the gas composition, the amount of rf power used will also determine the product. It is fortunate that the gas composition obtainable with our experimental apparatus is in the range for boron deposition, otherwise selection of gas composition from present information would be impossible.

**Power Input.** The power input to the glow is of great importance in determining the product and character of the product. The rf voltage at any gas composition and electrode geometry must be a value greater than the breakdown potential of the gases at that pressure. The rf current is a direct measurement of the ionization of the gases to produce electrons and positive ions. In electrochemical processing, these terms are or can be considered analogs of the redox potentials and current density, respectively. At higher currents, a faster coating rate will be attained, but changes in deposit characteristics will occur as a result of such changes in plating rate. Perhaps part of the nonuniformity of the deposit can be attributed to a nonuniform plating rate. The uniformity should be improved by moving the filament substrate through the glow.

**Pressure.** Since pressure is a concentration function, it may be expected to influence the type of deposit and the rate of deposition. At low pressures, needle-like deposits are observed. As the pressure is increased, the type of deposit changes and a coating or continuous layer is formed. Increasing the pressure further provides a smoother deposit. However as the pressure is increased the voltage necessary to maintain a glow discharge is increased.

**Post-Deposition Treatment.** One sample prepared at 30 mm Hg pressure, and at flow ratios and electrical conditions which normally provide a typical coating, was exposed to a hydrogen glow discharge before removal from the system. This was done to explore possible methods of reducing the brown, glassy material observed near the end of filaments. The treatment was done in 30 mm Hg  $H_2$  pressure and at low flow rates  $\sim 25$  cc/min. The rf current and dc voltage were 250 mA and 480 V respectively.

The glow was normal in every respect except that just outside the electrode on the downstream side a faint green fluorescence or glow was observed. The end areas of the sample did show some evidence of reduction. The most interesting part of the sample is shown in Fig. 6. This is a longitudinal cross section of a fracture. A very thin (less than 0.187-mil) layer is much darker than the bulk of the deposit. This has not been observed in any samples prepared during this process study.

### FILAMENT EVALUATION

**Density.** The density of filaments produced by this process has been measured by two techniques. A direct measurement was made by dropping a boron-coated pyrex rod in a density gradient tube. The average density was 2.24 gm/cc, which agrees satisfactorily with the value estimated from the density of boron, 2.35 gm/cc, and pyrex, 2.24 gm/cc.

An alternate indirect measurement has been performed during the process study by comparing the observed thickness of samples with that calculated-from-weight measurements. It was anticipated that the optically-measured value would be higher than the value calculated from weight measurements, which is an average value, since it is measured near the center of the filament.

This is observed in the data for samples 07-42 26A and B. The total thickness measured by optical methods are 2.2 and 2.4 mils, and calculated by weight the thicknesses are 1.45 and 1.72 mils. The results illustrate the nonuniformity of the static filament samples. However, the data is sufficiently in agreement to indicate that the filaments produced possess a density in accordance with the relative amounts of boron deposit and quartz substrate.

**X-Ray Identification.** A typical x-ray analysis is shown in Table VI. The diffuse lines observed in the x-ray pattern correspond to the alpha rhombohedral structure. This is the low-temperature form of boron. However, the structure is not well developed as indicated by the broad lines. The boron may have been in the process of changing from an amorphous structure to a crystalline structure at the time the experiment was terminated, or the crystalline boron was mixed with a matrix of amorphous boron.

Other samples of boron-coated 1.0-mil quartz filament show only two broad diffuse halos. No lines indicating  $B_2O_3$  were seen. No positive identification of the material was possible from the data.

**Tensile Strengths.** Several sample filaments of boron-coated 1-mil quartz substrate have been tested for ultimate strengths. No attempts have been made to obtain an elastic modulus since the samples prepared in the static apparatus are not of sufficient length. These data are presented in Table VII. The coating cracked and in some cases completely exfoliated. Thus, the values reported here basically represent breaking strengths of quartz rather than composite filament of boron-coated quartz monofilaments.

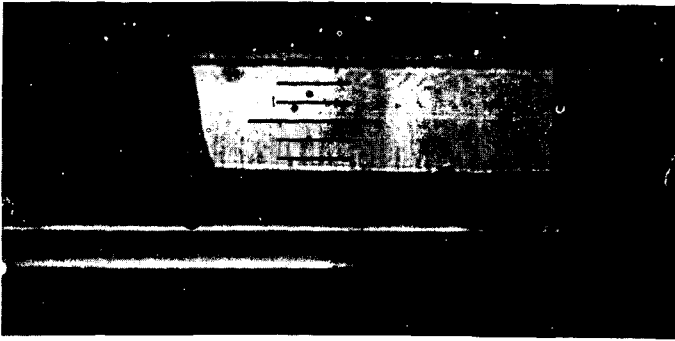
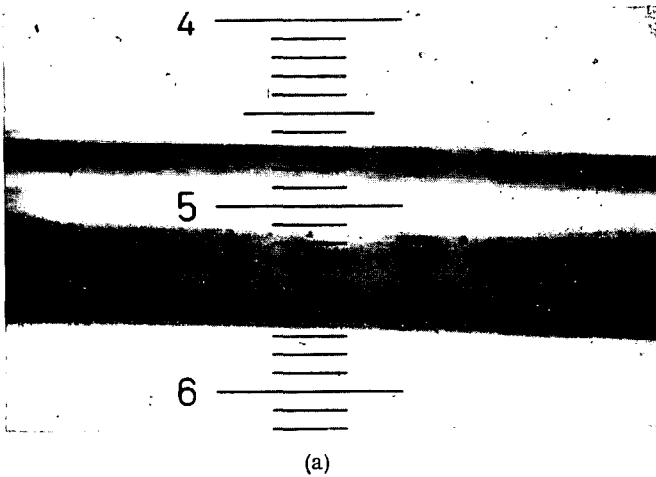
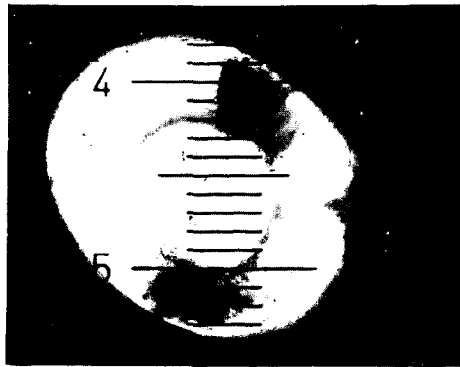


Fig. 6 Longitudinal Cross Section of Deposit After Exposure to  $H_2$  Glow Discharge



(a)



(b)

Fig. 7 (a) Longitudinal and (b) Cross Section of Boron-Coated Quartz Monofilament (220 $\times$ )

Table VI

## X-RAY DATA OF DEPOSIT

X-ray data		Deposited boron coating				
d	Unknown intensity	B <sub>2</sub> O <sub>3</sub>		Boron (a)		
		d	I/I <sub>o</sub>	d	I/I <sub>o</sub>	
6.0	Medium	6.08	35	4.07	100	
4.1	Strong (broad)	3.21	100			
3.2	Medium		2.55	70		
2.55	Strong (broad)	1.98			8	
1.95	Weak					
1.40	Very weak (broad)					

(a) Alpha rhombohedral form.

Table VII

## BREAKING WEIGHT OF SELECTED SAMPLES

Sample Number	Sample condition prior to test	Breaking weight (lb)	Filament diameter (mils)
07-40-24	Not observed	0.07	1.5
07-42-26	Not observed	0.07	1.5
07-52-36	Longitudinal cracks	0.11	2.0
07-53-36	Coating missing near tab	0.033	2.0

Coating Evaluation. A typical sample cross section prepared during the process study is shown in Fig. 7, demonstrating that a continuous coating can be successfully deposited. In the longitudinal cross section two mounds are fortuitously shown and it can be seen that the growth extends to the substrate. This indicates that the cause of this different growth originates at the substrate surface, possibly as a microcrack or particle of dust. The problem of handling the filament and its contamination would be minimized with use of a continuous system.

The bond between the coating and the substrate is essentially mechanical in nature. It would be very desirable to improve this by effecting some sort of reaction between the two materials to improve the overall properties of the filament. It would perhaps be undesirable to clean the organic or silicone finish from the substrate as has been done.

Microscopic examination of one of the filaments has revealed a possible explanation of the reduced strength of boron-coated quartz filaments. The pictures in Fig. 8 are typical of what is occasionally seen on samples. The chip and hole in the top and middle picture were not measured, but the rather deep cut made indicates that the quartz monofilament possesses weak portions that may separate before the bond between the boron and the quartz ruptures. These weak volumes contribute to the spread of the strength values observed earlier since they are probably randomly distributed. The hole and ball shown in the bottom figure have been measured during the microscopic examination. The ball was about 1.0 mil in diameter, the hole was observed to 0.8 mil, while the filament cross section averaged 1.8 mils. The coating thickness can be only 0.4 mil, so that the hole must have been formed by the loss of 0.4 mil of the quartz substrate.

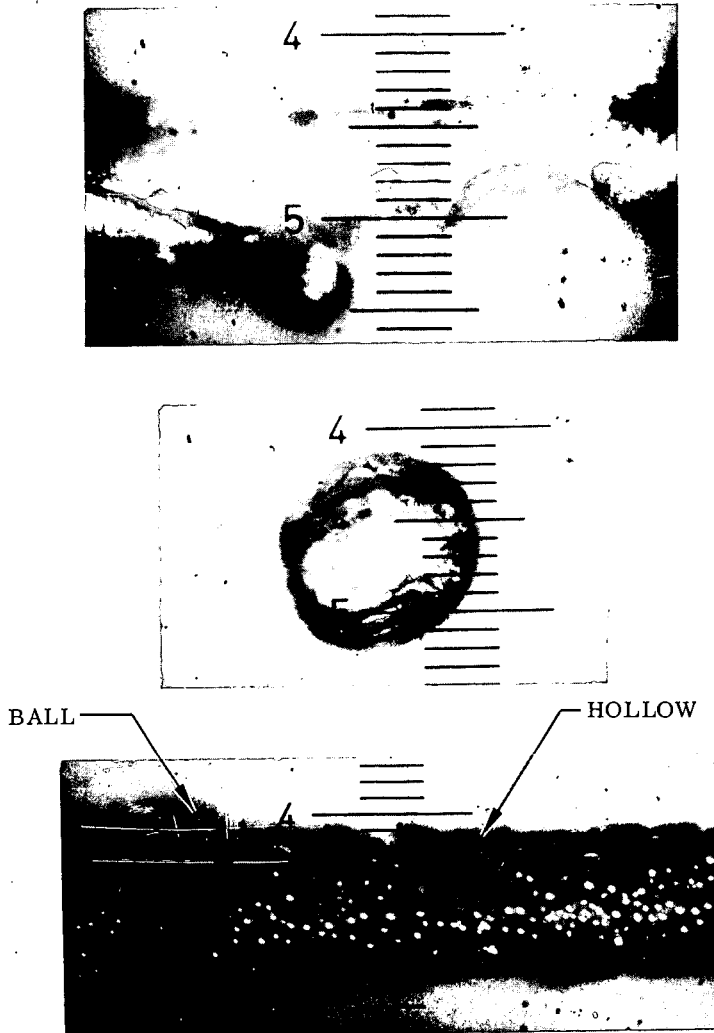


Fig. 8 Boron-Coated Quartz Monofilament ( $\times 340$ )

Top - Hollow in Boron-Coated Quartz Monofilament  
 Middle - Material From Hole  
 Bottom - Ball and Hollow in Thick Coating on Quartz Monofilament



Another source of weakness is the cracking and peeling. Many of these cracks and breaks are the result of handling during removal from the static apparatus. Use of a continuous filament moving through the apparatus and improvement in the adhesion of the coating to the substrate would possibly eliminate this problem.

### CONCLUSIONS

This paper basically represents a feasibility study of the deposition of boron from a glow discharge system produced in a boron trichloride-hydrogen medium. Feasibility of the basic concept has been conclusively demonstrated for dielectric or insulating substrates. It is probable that conditions can be adjusted to provide for deposition on metallic or conductive substrates as well. The following secondary conclusions can also be drawn from this work:

- Glow discharges can be initiated and sustained in hydrogen-boron trichloride mixtures at pressures of 50–100 mm.
- There is no apparent limit on coating thickness which can be deposited.
- The deposited boron is amorphous with a partial alpha rhombohedral crystalline character.
- Deposition rate is of the order of  $5 \times 10^{-5}$  gm/sec.
- Filament resistance increases with thickness; temperature in turn increases resulting in a higher deposition rate; this also results in increased bonding to the substrate by chemical or diffusive action.
- The process is quite sensitive to small amounts of impurities in the gas stream, particularly oxygen and moisture.
- The ratio of hydrogen to boron trichloride has a major effect on nature of the deposit; both sidewall deposition and downstream particle fallout increase with hydrogen concentration. However, the glow is more uniform at high hydrogen values, so these factors must be balanced for optimum performance.
- An increase in the boron trichloride to hydrogen ratio tends to concentrate the glow around the substrate, promoting efficiency and minimizing extraneous deposition.
- High hydrogen to boron trichloride ratios tend to produce boranes; operation at reduced rf currents tends to yield  $(BCl)_n$  polymers.

Current investigations are concerned with further development of the glow discharge deposition procedure to operate on a continuous basis utilizing moving filament techniques. Indications are that the technique may be used to prepare a high-quality boron filament at reasonable processing rates.

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